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TG-DSC-FTIR Analysis of Cyanobacteria Pyrolysis

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Abstract

Pyrolysis of cyanobacteria from Dianchi lake was investigated by TG-DSC-FTIR analysis at different heating rates (10, 20, 40 ℃/min). The results indicated that the pyrolysis of cyanobacteria can be divided into four stages: evaporation, depolymerization, devolatilization and carbonization. Meanwhile, the initial weight-loss temperature, weight-loss extreme position, endothermic and exothermic peaks were moved to higher temperature with the increaseing of the heating rate. The kinetic analysis was made with Popescu method. It indicated that the best kinetic model for the pyrolysis of cyanobacteria was the cylindrical symmetry of the phase boundary reaction model. The main pyrolysis gases checked with real-time online FTIR were HCN, NH3, CO, CO2, water vapor and hydrocarbons.

Keywords:cyanobacteria;TG-FTIR analysis;pyrolysis characteristics;kinetic;Popescu method

1.Introduction

As the major products of lake eutrophication, cyanobacteria is rich in lipids, protein, soluble carbohydrate biomass. Eutrophication is one of the most serious problems in China's lakes environmental protection[1]. Each summer to autumn, algae bloom appears in Dianchi Lake in Yunnan, Taihu Lake in Jiangsu and Chaohu Lake in Anhui in China , which not only seriously damages the environment, but also brings great negative impact to people's lives. Extensively distributed biomass is renewable, environment-friendly. Therefore, countries in the world are dedicated to developing bio- energy to replace or reduce non-renewable energy consumption, with the aim of reducing environmental pollution. Preparation of pyrolysis algae biofuels, not only achieves the purpose of turning waste into wealth, but also protects the environment.

At present, the study on pyrolysis of biomass with domestic and foreign scholars, mainly reflected in the analysis of pyrolysis characteristics, building kinetic model and proposing the corresponding pyrolysis mechanism [2-3]. With the rapid development of instrumentation in recent years, some scholars used the

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infrared spectrometry to detect and analyze the pyrolysis products in real time online [4]. For the pyrolysis of microalgae, the kinetic analysis was made with iso-conversional and master plots method by Zou Shuping ,etc[5] ,the results showed that the pyrolysis reaction can be dealt with as a single reaction model. In this paper, characteristics of cyanobacteria pyrolysis was analyzed by TGA-FTIR .At last, kinetics model was established and its pyrolysis products were detected and analyzed in real time online. All of these will provide a theoretical basis about cyanobacteria as well as microalgae thermochemical conversion and utilization.

2.Experimental

2.1.Materials

The raw materials used in this study (cyanobacteria) were collected from Dianchi Lake in Yunnan Province.The materials, after undergoing size-reduction by a chipper, was ground with a Wiley mill and screened. Particles smaller than 100 mesh were used for experiments. The powder was dried in an oven at 105 ℃for 4 h before use. The proximate, ultimate(dry basis) and the chemical compositions analysis results of the sample are given in Table1.

TABLE I. PROXIMATE ,ULTIMATE AND CHEMICAL COMPOSITIONS ANALYSIS RESULTS OF CYANOBACTERIA

Proximate analysis /%(wt)				Ultimate analysis/%(wt)					Chemical compositions analysis /%(wt)		
M_{ad}	A_{ad}	V_{ad}	FC_{ad}	C_{ad}	H_{ad}	O_{ad}	N_{ad}	S_{ad}	*fat*	*protein*	*total sugar*
1.7	7.94	76.45	15.61	45.30	6.92	27.63	10.02	0.62	5.48	57.9	20.05

2.2.Apparatus and method

Pyrolysis of the cyanobacteria powder was carried out in a TGA-thermogravimetric analyzer (NETZSCH,STA449F3).A sample mass of about 10 mg was used for thermogravimetric analysis that was conducted at heating rates of 10℃/min,20℃/min and 40℃/min,with a heating temperature range of 25–900℃, the data was automatically saved by computer during the process. Nitrogen and argon were used as the carrier gas and the protective gas at a flow rate of 60 ml/min,respectively.Pyrolysis gas products were analyzed by Fourier infrared spectrometer(BRUKER, VECTOR22) connected with TGA through a short stainless steel heated to 200℃ real-time on-line. In order to eliminate system error, we conducted a blank experiment of the same conditions after each experiment was done .

3.Results and discussions

3.1.pyrolysis characteristics analysis

Figure 1,2,3 are TG ,DTG,DSC curves during cyanobacteria pyrolysis at different heating rates. We could see that the variation of different curves is basically the same. The cyanobacteria pyrolysis is mainly divided into four stages. The first stage is evaporation (happened in the initial temperature to 130℃), TG curve falls slowly, with a small peak in DTG curve,and the weight-loss rate is about 2%. An endothermic peak in DSC curve is caused by evaporation. The second stage was depolymerization[6] (happened in 130-200℃),the main compositions of cyanobacteria are decomposed into oligomer or monomer, and TG, DTG, and the DSC curve has little change.The third stage is devolatilization (happened in 200-500℃),TG curve falls sharply, with a big peak in DTG curve, and weight-loss rate is more than 50%. The exothermic peak in DSC curve is due to the heat released by the decomposition of lipids, protein and soluble carbohydrate. The fourth stage is carbonization (happened in 500-900 ℃). TG curve falls slowly，and DTG curve is flat almost, a non-obvious exothermic peak in DSC curve, which symbolized the carbonization causes heat release.

The heating rate has great influence on pyrolysis,which is reflected in different thermogravimetric analysis curves. It is showed that the initial weight-loss temperature of TG curve is moved to higher temperature with the increasing of heating rate (from 10 ℃/min to 40℃/min), and burning residue gradually decreases(from 28.31% to 19.53%) in figure.1. We could see from the figure.2 and 3, the weight-loss extreme position of DTG curve and the endothermic or exothermic peak of DSC curve are moved to higher temperature, too. Because the process of pyrolysis is mainly controlled by dynamics and diffusion, and different stages mechanism are different. It is controlled by dynamics at low heating rate. But is controlled by diffusion at high heating rate, and heat-transfer lagging effect is more significant[7].

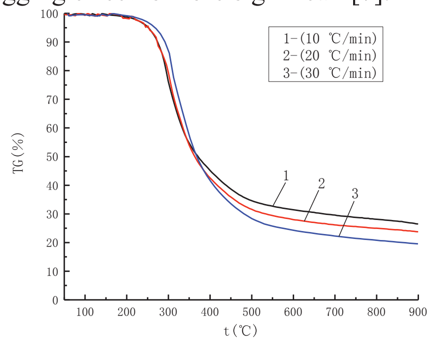

Figure 1. TG curves during cyanobacteria pyrolysis at different heating rates.

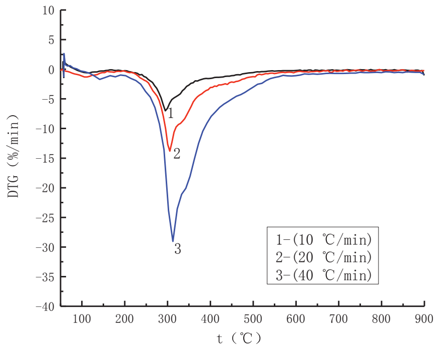

Figure 2. DTG curves during cyanobacteria pyrolysis at different heating rates.

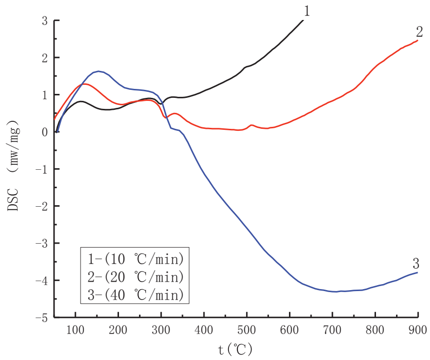

Figure 3. DSC curves during cyanobacteria pyrolysis at different heating rates.

3.2.Pyrolysis kinetic analysis

In this paper, $f(\alpha)$ and kinetic parameters(E and A) were gained by the Popescu method [8].

- *Determination of mechanism function f(α)*

The equation of reaction rate for the heterogeneous processes under non-isothermal conditions :

$$\frac{d\alpha}{dT} = \frac{1}{\beta} f(\alpha)K(T) \cdots\cdots\cdots\cdots (1)$$

Whereα,T, *f(α), β, K(T)* are conversion, temperature, differential form of mechanism function,heating rate, reaction rate constant, respectively.

The integral form of Eq. (1) is ,then

$$G_{mn} = \int_{\alpha_m}^{\alpha_n} \frac{dx}{f(x)} = \frac{1}{\beta}\int_{T_m}^{T_n} K(y)dy = \frac{1}{\beta} I_{mn} \cdots \quad (2)$$

Where α_m,α_n are two different degrees of conversion and T_m, T_n are their corresponding temperatures.

A plot of the values of G_{mn}versus 1/β has to lead to a straight line with an intercept of zero if the analytical form of *f(α)* is properly chosen. In practice, the best correlation coefficient can be used to choose the proper kinetic function.According to eleven different kinds of mechanism function[9], it was computed with experimental data by Popescu method. Correlation coefficients corresponding to various kinetic mechanisms for the plot G_{mn} versus 1/β were showed in table 2. The result showed that the best kinetic model for the pyrolysis of cyanobacteria was the cylindrical symmetry of the phase boundary reaction model(R2), the differential expression of mechanism function f(α)= 2（1-α）$^{1/2}$, the integral expression G(α)= 1-（1-α）$^{1/2}$.

- *Calculation of the kinetic parameters*

Making an assumption *that K*（*T*）obeys an Arrhenius-type relationship:

$$K(T) = A\exp(-E/RT) \cdots\cdots\cdots\cdots (3)$$

Where E and A are the activation energy and the pre-exponential factor.

Put Eq. (3) into Eq. (2), after using the first mean value theorem for definite integrals and taking the logarithms, and rearranging the terms thus to write:

$$\ln\frac{\beta}{T_n - T_m} = \ln\frac{A}{G_{mn}} - \frac{E}{RT_\zeta} \cdots\cdots\cdots\cdots (4)$$

Where $T_\zeta=(T_n+T_m)/2$.

Put experimental data and the best kinetic mechanism into Eq. (4), the plot of ln $[\beta/(T_n-T_m)]$ versus $1/T_\zeta$ was drew, and linear fitting by origin software. The activation energy E and the pre-exponential factor A were calculated by the slope and intercept of fitted curve. The results were showed in table 3. In the earlier of the main stage (α between 0.1-0.3), weak bonds of the polymers have been almost broken into low polymer and monomer molecules after depolymerization, the activation energy is about 188 kJ/mol. In the mid of the main stage (α between 0.3-0.6), covalent bonds of low polymer and monomer molecules have been most broken into small molecular, and produced a lot of free radical, while the activation energy has increased to about 234 kJ/mol. In the later of the main stage (α between 0.6-0.9), this process continues to generate free radicals, and activation slightly increases to 240 kJ/mol[10].

TABLE II. CORRELATION COEFFICIENTS CORRESPONDING TO VARIOUS KINETIC MECHANISMS FOR THE PLOT GMN VS 1/B

Model code	**T_m=473.256K T_n=573.372K**	**T_m=573.372K T_n=673.147 K**	**T_m=673.147 K T_n=773.460 K**	**T_m=773.460 K T_n=873.809 K**
F1	0.997490	0.989848	0.976876	0.953523
F2	0.993718	0.989147	0.794327	0.876170
F3	0.990478	0.982717	0.216764	0.824190
A2	0.902423	0.980611	0.991145	0.970510
A3	0.743468	0.975437	0.993950	0.975930
R1	0.999948	0.983233	0.999328	0.985027

R2	**0.999065**	**0.987645**	**0.991298**	**0.992570**
R3	0.998595	0.988603	0.990393	0.981390
D1	0.119912	0.995490	0.992365	0.993895
D2	0.967695	0.995580	0.988794	0.997430
D3	0.969478	0.994538	0.962341	0.960650

TABLE III. KINETIC PARAMETERS OF CYANOBACTERIA PYROLYSIS

αn –αm(%)	E(kJ/mol)	A(1/s)	Correlation coefficient
0.3-0.1	188.961	2.42247×10^{16}	-0.993488
0.6-0.3	234.437	1.65425×10^{19}	-0.999987
0.9-0.6	240.248	3.52292×10^{19}	-0.999999

3.3.FTIR analysis of pyrolysis cyanobacteria

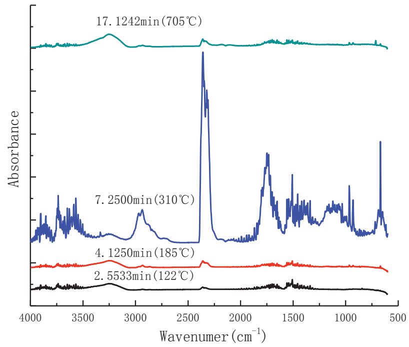

Figure 4. FTIR spectral plot of gases produced at different time from pyrolysis of cyanobacteria at heating rate of 40℃/min .

Figure.4 is the corresponding FTIR spectral plot at four typical moments. From Figure.4, at the initial stage of pyrolysis, there are wave numbers 3964～3500cm^{-1}、1800～1300 cm^{-1}corresponding to the water steam absorption peaks at 2.5533 min (122℃), this phenomenon anastomoses with the stage of water drying. At 4.1250min (185℃), the water steam absorption peaks weakened, appearing alkane hydrocarbon gases peaks 3100～2750 cm^{-1} and obvious characteristic peak of CO_2 2375～2250cm^{-1}, this stage is called depolymerization. At the major stage of pyrolysis, there are much more strong peaks at 7.25min（310℃）, 3964～3500cm^{-1} corresponding to the water steam absorption peak, 1000～730 cm^{-1} corresponding to NH_3 characteristic peak , there is HCN characteristic peak at 3300cm^{-1} more or less[11], so as to CO characteristic peak at 2120cm^{-1} more or less, 2375～2250 cm^{-1}、730～560 cm^{-1} corresponding to the CO_2 characteristic peak. There is the biggest absorbance between 2375～2250 cm^{-1} corresponding to the maximum weight-loss rate in DTG curve, there are sorts of alkane, aldehydes and ketones, carboxylic acid and glycol and macromolecular substances at 3100～2750 cm^{-1}、1850～1580 cm^{-1}、1580～1000 cm^{-1}[12] , and these products are from the decomposition of cyanobacteria ingredient of lipids, protein and soluble carbohydrate. At the last stage of pyrolysis, H_2O and CO_2 characteristic peak are very weak, and there are a spot of CO and alkane hydrocarbon gases at 17.1242min（705℃）,which is caused by the further carbonization of C—H and C—O bonds.

4.Conclusions

- The pyrolysis of cyanobacteria can be divided into four stages:water drying, depolymerization, devolatilization and carbonization.

- The best kinetic model for the pyrolysis of cyanobacteria was the cylindrical symmetry of the phase boundary reaction model(R2).
- The main pyrolysis gases checked with real-time online FTIR were HCN, NH_3, CO,CO_2,water vapor and hydrocarbons.

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References

[1] Peng Weimin, Li Xiangshu, Wu Qingyu, Ge Yueyun, "Recovery of planktonic algae f rom lakes to produce fuels by pyrolysis," Techniques and Equipments for Environmental Pollution Control.China, vol.1,pp.24-28,June 2001.

[2] Taro Sonobe, Nakorn Worasuwannarak,"Kinetic analyses of biomass pyrolysis using the distributed activation energy model,"Fuel.America,vol.87,pp. 414-421,January 2008.

[3] Lai Yanhua, Lv Mingxin, Ma Chunyuan, Shi Mingheng ,"Study on the characteristics and dynamics of pyrolysis process agricultural residues,"Acta Energiae Solaris Sinica.China,vol.23,pp. 203-206,April 2002.

[4] Seong-Beom Lee , Oladiran Fasina, "TG-FTIR analysis of switchgrass pyrolysis,"Journal of Analytical and Applied Pyrolysis. America,vol.89,pp.39-43April 2009.

[5] Zou Shuping, Wu Yulong Yang Mingde,Zhang Jianan, Li Chun, Tong Junmao, "Characteristics and dynamics of pyrolysis process microalgae," Journal of Combustion Science and Technology.China,vol.13,pp. 330-334 ,August 2007.

[6] Kong Xiaoying,Li Lianhua, Yin Xiuli, Sun Yongming, Ma Longlong, Yuan Zhenhong, Liu Shuwei, "Experiment on pyrolysis product and pyrolysis characteristics of marine alga with high ash content,"Acta Energiae Solaris Sinica.China,vol.31,pp . 536-539,May 2010.

[7] Wu Jingli,Wang Congwei, Yin Xiuli, Wu Chuangzhi, Ma Longlong, Zhou Zhaoqiu, Chen Hanpin, " Study on pyrolysis of heavy fractions of bio-oil by using TG-FTIR analysis,"Acta Energiae Solaris Sinica.China,vol.31,pp. 113-119,January 2010.

[8] Popescu C, "Integral method to analyze the kinetics of heterogeneous reactions under non-isothermal conditions:A varianton the Ozawa-Flynn-Wall method,"Thermochimica Acta. America,vol.285,pp.309-323 February,1996.

[9] L.T. Vlaev, I.G. Markovska, L.A. Lyubchev, "Non-isothermal kinetics of pyrolysis of rice husk,"Thermochimica Acta. America,vol.406,pp.1-7,January 2003.

[10] V. Mamleev, S. Bourbigot, M. L. Brasb, J.Yvonc, J. Lefebvreb, "Model-free method for evaluation of activation energies in modulated thermogravimetry and analysis of cellulose decomposition,"Chem. Eng. Sci. America,vol.61,pp.1276-1281,July 2006.

[11] J. Giuntoli , W. de Jong , S. Arvelakis , H. Spliethoff , A.H.M. Verkooijen, "Quantitative and kinetic TG-FTIR study of biomass residue pyrolysis:Dry distiller's grains with solubles (DDGS) and chicken manure," Journal of Analytical and Applied Pyrolysis. America,vol.85,pp.301-312, December 2009.

[12] Wang Shurong, Liu Qian, Luo Zhongyang,Wen Lihua,Cen Kefa, "Mechanism study of cellulose pyrolysis using thermogravimetric analysis coupled with infrared spectroscopy," Journal of Zhejiang University(Engineer Science).China,vol.40,pp. 1154-1162,July 2006.